Cooperative Dynamics in Hydrogen Bonded Liquids: A Dielectric Spectroscopy Approach

Synopsis

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SWAMI RAMANAND TEERTH MARATHWADA UNIVERSITY, NANDED

For the registration of the topic for
Doctor of Philosophy
in the subject of **PHYSICS**
(Faculty of Science)

(Mr Prakash Bhadane)
Research Student
Saraswati College of Engineering,
Kharghar, Navi Mumbai

(Dr Y S Joshi)
Research Guide,
Assistant Professor,
LBS Mahavidyalaya,
Dharmabad.
(Mobile: 9405362172)

Abstract of proposed work plan/problem:

"Cooperative Dynamics in Hydrogen Bonded Liquids: A Dielectric Spectroscopy Approach"

1. Introduction:

The molecular relaxations among the hydrogen bonded liquids are due to the contribution of dynamical processes. The dynamical process may be intramolecular and intermolecular oscillations, single particle dynamics, and cooperative rearrangement of the hydrogen bonded system [1]. The dielectric relaxation spectroscopy (DRS) useful to study the cooperative rearrangement of the hydrogen bonded liquids. In comparison with the other techniques (IR, NMR), DRS is especially advantageous for an investigation of the cooperative nature of hydrogen bonded liquids because it monitors the collective motion of a molecular ensemble through the response of the total dipole moment of the sample to a time dependent electric field [1]. The dielectric spectroscopy describes the complex permittivity spectra, $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$, of the liquids. In order to study these molecular interactions among the hydrogen bonded liquids and their mixtures, DRS has proven its applicability for measurement of dielectric properties in a plethora of research papers [1-11,16-25].

In this present work, it is proposed to measure the complex permittivity spectra at various frequency ranges of the hydrogen bonded liquids and their binary mixtures. Further, these permittivity spectra will be used to obtain the dielectric properties of binary mixtures of hydrogen bonded liquids in order to understand the significance of molecular interaction in them through cooperative dynamics.

2. Review of Literature and Development in the subject (Previous work done in the relevant area)

For the dielectric characterization of the liquid samples a wide range of frequency spectra is used known as Broadband Dielectric Spectra (BDS) [11]. In literature survey, there are various techniques for the dielectric measurement in the BDS. Generally, the measurement techniques are broadly classified in two ways, Frequency Domain and Time Domain. In frequency domain LCR meter, Network Analyzer and Impedance spectroscopy techniques are useful for the dielectric measurement at different frequency ranges. The later technique is time domain also known as time domain reflectometry (TDR) technique used for the dielectric measurement used from some few MHz to GHz frequency range. Depending upon the frequency of dielectric relaxation of molecules suitable technique can be selected for the experimental set up. The dielectric measurement at low frequency range from 20Hz to 1MHz using LCR meter for polar, non polar and their binary mixtures have been carried out by Sengwa et.al. [12-15]. In this measurement technique, using the dielectric cell the capacitance with and without samples are recorded. The permittivity has been evaluated using the ratio of these capacitances. The TDR dielectric measurement system consists of a high frequency step generator which produces fast rising pulse of the order of picoseconds. A train of suitable fast rising pulses is applied to a coaxial transmission line of characteristic impedance of 50Ω. The literature survey shows that the experimental setup for time domain technique with various frequency ranges (upto 10GHz, 20GHz and 30GHz) has been successfully developed. S. Mashimo et. al. have find out the complex permittivity of aqueous solutions by time domain reflectometry [2]. Cole et. al.[3] had developed the time domain reflection methods for the dielectric measurement up to 10 GHz. The Bertolini et. al. [4] developed bilinear calibration method for the accurate measurement of the dielectric parameters of highly polar liquids, dilute solutions of polar molecules in non polar solvents and electrolyte solutions.

Mehrotra et. al. [5] developed the TDR measurement system in India first time for the measurement of polar and non polar solutions up to 10GHz. The hydrogen bonding behavior of aqueous alcohols was extensively studied by Sato et. al., Yagihara et. al. and Mashimo et. al. through the dielectric properties, heterogeneous interactions and cooperative domains (CD) [6-10]. In recent times, Kumbharkhane et.al. [16-21, 23-25] set up a TDR technique for the measurement of the complex permittivity at various temperatures upto 30 GHz. This technique is useful for the measurement of complex permittivity spectra of various polar, non-polar and binary mixtures of these systems. During last few decades this technique is extensively used to study structural behavior of hydrogen bonded liquids such as alcohols, diols, Polyhydric sugar alcohols, biomolecules, polymers, glycol ethers etc. at various frequency ranges [1-26]. These studies provide vital information on the molecular configuration of a system. High frequency molecular behavior of hydrogen bonded liquids provides information regarding their molecular interactions and dynamics and structural changes in the molecules, involved at the dipolar levels.

3. Objectives of Research/Proposed hypothesis:

- To measure the accurate dielectric permittivity spectra of the hydrogen bonded liquids in pure and mixture form.
- To evaluate the dielectric parameters such as static dielectric constant, relaxation time, high frequency dielectric permittivity by using suitable empirical model Debye, Cole-Cole or Cole-Davidson.
- To measure the refractive indices of hydrogen bonded liquids.
- To study cooperative dynamics in these systems using the dielectric properties.

4. Methodology

To study the dielectric behavior of solids, liquids and gaseous materials over a frequency range extending from D.C. and low frequencies through RF and microwave lengths to far IR there are various measurement techniques. It must be determined by the material to be studied and the frequency interval of interest. The dielectric properties of molecules and their binary mixtures can be determined by using 'capacitive measurement method' at lower frequencies from few Hz to MHz. The capacitances of the Liquid Dielectric Test Fixture with and without samples were measured by using it for a short compensation. The Test Fixture correction coefficient was also considered to cancel the stray capacitance during the determination dielectric constant values.

The high frequency dielectric measurement can be performed using Time Domain technique, generally known as time domain reflectrometry (TDR). The TDR technique consist of three major elements a fast rising tunnel diode pulse generator, a wide band sampling oscilloscope and a data-acquisition system. A step voltage pulse is passed into the test liquid and it is monitored and recorded by the sampling oscilloscope. The reflected pulses with and without samples are then compared [as a function of time]. By means of a suitable mathematical transformation, the frequency response of the sample can be calculated. Time-domain methods have some advantages over frequency domain methods. Since the dielectric response is recorded in the time domain, one measurement covers a wide frequency range. This method can measure the complex permittivity not only in the microwave range but also in the radio frequency range. The instrumentation set up is quite simple and is less expensive than that used in frequency domain methods. Dielectric constant at optical frequency can be derived from the square of refractive index of the liquid. The refractive index of the liquid sample can be measured using Abbe's refractometer.

5. Importance of study/society application:

The following scientists are doing research in this field at national/international level

- **International status:**

1. S Yagihara, University of Tokyo, Tokyo, Japan
2. R Buchner, Institute of Physical and Theoretical Chemistry, University of Regensburg 93040 Regensburg, Germany.
3. Y Feldman, Department of Applied Physics, The Hebrew University of Jerusalem, 91904, Jerusalem, Israel.
4. T Sato, Division of Pure and Applied Physics, Graduate School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
5. A Catldo, Universita di Lecce, via Monteroni, 73100 Lecce, Italy
6. Udo Kaatze, Drittes Physikalisches Institut Georg-August-Universität Göttingen, Germany.

- **National Status:**

1. S C Mehrotra, Dr. BAMU, Aurangabad (MS).
2. R J Sengwa, JNV University, Jodhpur, Rajasthan.
3. A C Kumbharkhane, SRTM University, Nanded (MS).
4. V A Rana, Gujarat University, Ahmadabad (Gujarat).

- **Significance of the study**

The dielectric properties of associating liquids are very remarkable. They typically display extremely high permittivity at low frequencies, their frequency dependence permits identification and investigation of a number of completely different underlying mechanisms, and hence, dielectric studies of biomaterials have long been important in biophysics.

The natural observable fact involves the interaction between matter and energy. The nature and strength of molecular interactions in soft matter have been established as the cause for the behavioral change in chemical compounds. The extent of recognition of the most suitable and strongly proven structures involving certain chemical bonds and interactions are based on quite a number of qualitative and quantitative tests utilizing independent physical methods. IR, NMR, Ultrasonic and Dielectric Spectroscopy are a few among them. Dielectric relaxation studies will throw light on actual functioning of molecule. The dielectric spectroscopy method occupies a special place among the numerous modern methods used for physical and chemical analysis of material, because it enables investigation of dielectric relaxation processes in an extremely wide range of characteristics time.

6. Proposed work plan/Formulation and structure of study:

- **First Year:** In detail, the literature survey regarding the research problem will be done. To study the theoretical background of the research problem. Then choose the appropriate hydrogen bonded liquids for the dielectric measurements.

- **Second Year:** Actual experimental work will be carried out for the measurement of dielectric relaxation mechanism of these hydrogen bonded liquids at different frequency ranges. To obtain the dielectric properties such as static dielectric constant, relaxation time dielectric constant at high frequency for these systems by fitting the experimental data in suitable model. To measure the refractive indices of these liquids.

- **Third Year:** Dielectric information extracted from data analysis of these systems will be used further for interpretations of molecular behavior through cooperative nature. These interpretations will be published by writing research papers or presenting the work in conference/seminars. Finally, write up thesis and complete the research work.

7. References:

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Mr Prakash Bhadane
Research Student

Dr Y S Joshi
Research Guide